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Three-dimensional model evaluation of the Ozone Depletion Potentials for n-propyl bromide, trichloroethylene and perchloroethylene

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Abstract

The existing solvents trichloroethylene (TCE) and perchloroethylene (PCE) and proposed solvent n-propyl bromide (nPB) have atmospheric lifetimes from days to a few months, but contain chlorine or bromine that could affect stratospheric ozone. Several previous studies estimated the Ozone Depletion Potentials (ODPs) for various assumptions for location of nPB emissions, but these studies used simplified modeling treatments. The primary purpose of this study is to reevaluate the ODP for nPB using a current-generation chemistry-transport model of the troposphere and stratosphere. For the first time, ODPs for TCE and PCE are also evaluated. Emissions representing industrial use of each compound are incorporated on land surfaces from 30° N to 60° N. The atmospheric chemical lifetime obtained for nPB is 24.7 days, similar to past literature, but the ODP is 0.0049, lower than in past studies. The derived atmospheric lifetime for TCE is 13.0 days and for PCE is 111 days. The corresponding ODPs are 0.00035 and 0.0060, respectively.

1 Introduction

n-Propyl bromide (chemical formula $CH_3CH_2CH_2Br$, also named 1-bromopropane and abbreviated below as nPB) has been proposed as a potential replacement for compounds that have been used as solvents for many years including trichloroethylene (TCE) and perchloroethylene (PCE). As discussed in the 2002 World Meteorological Organization international stratospheric ozone assessment (Ko et al., 2003), four modeling studies (Wuebbles et al., 1999, 2001; Bridgeman et al., 2000; Olsen et al., 2000) have previously evaluated Ozone Depletion Potentials (ODPs) for nPB. These studies used the modified concept for ODPs that accounts for the location of emissions (Wuebbles and Ko, 1999) as compared to the original definition developed for longer-lived gases. However, none of the nPB studies evaluated the ODPs using a three-dimensional chemistry-transport model of the troposphere and stratosphere with

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complete representation of relevant chemistry processes. The purpose of this study is to update the ODPs for nPB using such a model. In addition, ODPs of TCE and PCE are also evaluated for the first time, though the primary environmental concerns about these compounds relate to their toxicity, as summarized in OEHHA (1999, 2000).

In the earlier nPB studies, Wuebbles et al. (1999) used a zonally-averaged two-dimensional (2-D) model to estimate ODP. Olsen et al. (2000) applied the low-resolution (8° latitude × 10° longitude × 9 layers) three-dimensional (3-D) UCI tropospheric chemical-transport model to determine the amount of very short-lived (VSL) substances for a range of atmospheric lifetimes, and for various seasons and latitudes of emission, reaching the tropical tropopause. Then by scaling the ODP values from 2-D model results (Wuebbles et al., 1999), they estimated ODP values for nPB ranging from 0.0002 (for summer emissions at 56° N to 64° N) to as large as 0.06 for tropical emissions. Bridgeman et al. (2000) used the TOMCAT 3-D global chemical-transport model (5.6° × 5.6° × 31 levels) to evaluate the atmospheric lifetime and amount of nPB reaching the stratosphere as a function of location and season of emission. They calculated ODPs empirically, based on the derived lifetime and the fraction of nPB emissions reaching the stratosphere. For nPB, they derived ODPs that vary from 0.0033 for emissions from Europe to 0.0109 for emissions from Indonesia. The study assumed that any bromine atoms released in the troposphere would be removed by rainout with 100% efficiency before reaching the stratosphere. Thus, their derived ODPs only considered the direct nPB reaching the stratosphere.

Wuebbles et al. (2001) used the MOZART-2 3-D chemical-transport model (5° × 5° × 34 levels) in combination with studies using their 2-D model in examining the potential effects of nPB on stratospheric ozone and the corresponding set of ODPs for nPB, and attempted to quantify degradation product effects. With available information, bromoacetone (BrAc) was the intermediate degradation product which had the largest concentration and had a local photochemical lifetime more than 1 day. For nPB emitted equally over global land masses north of 60° S and south of 70° N, their 3-D model calculations suggest that about 0.44% of the emitted bromine enters the stratosphere.

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About 33% of the bromine reaching the stratosphere results from the direct transport of nPB to the stratosphere and about 19% due to the transport of BrAc to the stratosphere. The rest (48%) is from transport of inorganic bromine.

These studies demonstrated the importance of considering both pathways in deriving the halogen reaching the stratosphere and the resulting ODPs for VSL gases like nPB. Although the Wuebbles et al. (2001) study included both pathways, one can derive ODP values for situations more comparable to the other studies by considering only the nPB reaching the stratosphere. When that is done, the range of ODP values for the emission scenarios considered is 0.003 (for US emissions) to 0.03 (for Indonesia and S.E. Asia), comparable to the values determined by Olsen et al. (2000) and Bridgeman et al. (2000). The range of values in Olsen et al. was due to separate results for individual seasons.

Measurements by Burkholder et al. (2002) suggest that the local lifetime of BrAc is a few hours rather than at least one day as assumed in Wuebbles et al. (2001). Ko et al. (2003) modified the Wuebbles et al. (2001) ODP values to account for this overestimate of the BrAc atmospheric lifetime. For nPB emissions at midlatitudes (North America, Europe, and Asia – roughly 30° N to 60° N), the modified ODPs range from 0.017 to 0.026.

Since the earlier studies were published, much more has been learned about the oxidation of nPB and the chemistry of nPB degradation products in the atmosphere. In addition to the Burkholder et al. (2002) study of BrAc, there have been new measurements and analyses of nPB reaction with OH (Gilles et al., 2002; Martínez-Avilés et al., 2008a) and of the specific reactions and reaction rates in the reaction mechanism after initiation (Martínez-Avilés et al., 2008b). We have incorporated these new findings into the reaction mechanism used in the modeling studies.

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2 Methodology

The ODP concept (Wuebbles, 1981, 1983) arose as a means of determining the relative ability of a chemical to destroy stratospheric ozone. ODPs are an integral part of national and international considerations on ozone-protection policy, including the Montreal Protocol and its Amendments and the US Clean Air Act. ODPs provide an important and relatively straightforward way of analyzing the potential for a new chemical to affect ozone relative to the CFCs, Halons, and other replacement compounds. ODPs are currently determined by two different means: calculations from chemistry-transport models of the global atmosphere (CTMs), and calculations using a semi-empirical approach (Solomon et al., 1992).

An ODP is a relative measure of the expected cumulative effect on stratospheric ozone per unit mass emission of a gas compared with the expected effect from the same mass emission of CFC-11. Therefore, it is defined as the change in total ozone per unit mass emission of the gas, relative to the change in total ozone per unit mass emission of CFC-11. ODP by itself does not, however, indicate the actual emissions or the amount of ozone depletion that has occurred or might occur.

Traditionally, zonally averaged 2-D CTMs were used for calculating the ozone response in the stratosphere. Past ODP evaluations were conducted for chemicals with atmospheric lifetimes more than approximately one year. Such long-lived gases mixed well throughout the troposphere after surface release, and large fractions of the surface emissions reached the stratosphere. However, many of the compounds now being considered either for new applications or as replacements for substances controlled under the Montreal Protocol are designed to be short-lived, on the order of days to a few months, so as to reduce the impacts on ozone and climate. These short-lived replacement gases still can be vertically transported into the lower stratosphere by intense convection in the tropical troposphere, which is relevant to possible effects on ozone from these compounds. Thus, the ODP of a VSL species depends upon its distribution in the atmosphere and the location of its source (Wuebbles and Ko, 1999; Wuebbles et

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al., 2001; Ko et al., 2003). Unfortunately, the determination of ODPs for these gases is not straightforward because their short atmospheric lifetimes leave them poorly mixed in the troposphere. Also, the traditional 2-D model analysis of ODPs is not sufficiently accurate to calculate the integrated amount of the halogenated VSL source and reaction product gases in the troposphere that enter the stratosphere (Wuebbles et al., 2001).

3-D CTMs representing the complete troposphere and stratosphere are necessary for evaluating the halogen loading and ozone depletion in the stratosphere for VSL species. Thus the definition of ODPs has been revised for VSL compounds (Wuebbles et al., 2001; Ko et al., 2003). The new ODP definition for the VSL compounds accounts for the variation that can occur in the ODP as a function of where and when the compound is used and emitted. The most important factor in evaluating the ODP of VSL compounds is shown to be latitude distribution of the surface emissions because halogens from source gases emitted at higher latitudes are less likely to reach the stratosphere than from source gases emitted in the tropics (Bridgeman et al., 2000; Olsen et al., 2000; Wuebbles et al., 2001). 3-D CTMs, which include a much more comprehensive treatment of transport than available for 2-D models, are now preferable for calculations of ODPs both for the longer-lived gases and for the very short-lived candidate replacement compounds. These models can not only determine the amount of the substance reaching the stratosphere directly but can also follow the processes affecting the reaction products. Studies suggest that the vast majority of chlorine or bromine reaching the stratosphere from VSL substances is transported there in reaction products (Wuebbles et al., 2001; Ko et al., 2003; Law et al., 2007).

This study uses the current-generation 3-D model of global atmospheric chemistry and physics developed by the National Center for Atmospheric Research (NCAR) called the Model for OZone And Related Tracers version 3.1 (MOZART-3). MOZART-3 has been used to explicitly calculate the impact of halocarbon emissions added at the Earth's surface into the atmosphere on ozone depletion. The MOZART-3 CTM includes a complete representation of tropospheric, stratospheric, and upper

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atmospheric processes (Kinnison et al., 2007). It incorporates a full stratosphere, including the chemistry of chlorine species (Cl_y) and bromine species (Br_y) important in stratospheric ozone calculation as well as updated hydrogen, nitrogen, and hydrocarbon oxidation chemistry relevant to stratospheric and tropospheric chemistry included in the lower atmospheric version, MOZART-2 (Horowitz et al., 2003). Representations of relevant heterogeneous and physical processes for winter/spring polar vortex related to ozone destruction are also fully included in the model. This model has been evaluated extensively via comparisons with measurements of atmospheric trace gases from satellite data and measurement campaigns (e.g., Wei et al., 2003; Pan et al., 2007).

In this study, the initiating reaction of nPB with OH radical is based on the rate constants from Gilles et al. (2002):

$$k(\mathrm{nPB + OH \rightarrow CH_3CH_2CHBr + H_2O}) = 1.44 \times 10^{-12} \exp(-450/T) \quad (1a)$$

$$k(\mathrm{nPB + OH \rightarrow CH_3CHCH_2Br + H_2O}) = 2.54 \times 10^{-18} T^2 \exp(265/T) \quad (1b)$$

$$k(\mathrm{nPB + OH \rightarrow CH_2CH_2CH_2Br + H_2O}) = 2.89 \times 10^{-12} \exp(-957/T) \quad (1c)$$

where the temperature T is in K and rate constants k are in $\mathrm{cm^3\,molec^{-1}\,s^{-1}}$. Analysis of the subsequent reactions by the radicals produced by OH reaction with nPB from Martínez-Avilés et al. (2008a, b) suggests that the only organobromine degradation product to have a significant lifetime against further reaction and to be produced in a significant fraction of the nPB input to the atmosphere is BrAc, $CH_3C(O)CH_2Br$. The BrAc absorption cross sections and photolysis quantum yields of Burkholder et al. (2002) are used in this study.

The chloroalkenes PCE and TCE are expected to react in the atmosphere primarily by addition of OH radical to the C=C double bond. The rate constants for these addition reactions are taken as the high-pressure limit expressions from the JPL 2006 photochemical data evaluation by Sander et al. (2006):

$$k(\mathrm{PCE + OH}) = 4.7 \times 10^{-12} \exp(-990/T) \quad (2)$$

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$$k(\mathrm{TCE}+\mathrm{OH})=8.00\times10^{-13}\exp(300/T) \quad (3)$$

where the temperature T is in K and rate constants k are in $\mathrm{cm}^3\,\mathrm{molec}^{-1}\,\mathrm{s}^{-1}$. The PCE + OH rate constant expression in the IUPAC photochemical data evaluation (Atkinson et al., 2008) agrees with that in Sander et al. (2006) to within 6% for T of 200 to 300 K. The TCE + OH rate constant expression from Atkinson et al. (2008) agrees with that given by Sander et al. (2006) for T of 240 to 300 K; while the IUPAC values are more than 10% higher for T below 240 K, this is not expected to produce much difference in the TCE lifetime because limited amounts of TCE reach colder temperatures in the upper troposphere (see Fig. 4a below).

Radicals produced by OH addition to PCE or TCE then are likely to add O_2, then react with NO to produce chlorinated hydroxyalkoxy radicals. In this study, we have approximated the subsequent chemistry as release of all chlorine within one time step. The chlorinated hydroxyalkoxy radicals are likely to produce phosgene (CCl_2O) for both TCE and PCE and chloroformaldehyde (CHClO) for TCE, which react further by both OH and photolysis under daytime conditions suitable for oxidation of PCE or TCE.

Chemical reaction-rate constants and photochemical data for reactions other than those of nPB, TCE, and PCE follow the recommendations of Sander et al. (2003). The MOZART-3 CTM is driven by meteorology fields derived from the Whole Atmosphere Community Climate Model (WACCM) version 1b (Sassi et al., 2004). MOZART-3 thus has a 2.8° resolution in latitude and longitude and a hybrid sigma-pressure vertical coordinate including 66 layers from the surface to 5.1×10^{-6} hPa (approximately 140 km).

We evaluate the atmospheric lifetimes and ODPs for the three compounds in the MOZART-3 CTM. A steady-state background atmosphere corresponding to the year 2000 was derived assuming fixed surface mixing ratios for long-lived gases (such as nitrous oxide, methane, chlorofluorocarbons, and other halogenated source gases) and fixed emissions for short-lived gases. Separate studies were then completed with added emissions of each compound, with a separate analysis done for CFC-11 (for derivation of the denominator in the ODP), to give a small, less than one percent, decrease in globally-averaged ozone. Emissions of nPB, TCE, and PCE were assumed

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to occur entirely on land at midlatitudes in the Northern Hemisphere, from 30° N to 60° N (which corresponds to where the vast majority of current or future emissions are also expected to occur). In addition, for nPB the atmospheric lifetime and ODP was determined assuming emissions evenly distributed over land globally, from 60° S to 70° N.

3 Results

ODP calculation in an atmospheric CTM requires two perturbation runs for comparison to the CTM reference atmosphere: a CFC-11 ($CFCl_3$, also known as trichlorofluoromethane) run and a run incorporating the compound under evaluation. Each CTM perturbation is run to steady state, after which the change in total ozone burden in the atmosphere and the flux of the substance causing the ozone change are calculated for the CFC-11 run and for the run of the compound under study.

The nPB flux used to illustrate industrial use is a rate of 8.64×10^8 molecules cm^{-2} s^{-1} from all land at latitudes 30° N to 60° N, for a total nPB emission rate of 2.48 Tg yr^{-1}. That flux resulted in a global O_3 burden decrease of 0.214%, of which 0.123% was above the tropopause. Figure 1 shows the derived annual and zonal average distribution of nPB, the corresponding distribution of BrAc and change in Br_y, and the resulting change in the distribution of tropospheric and stratospheric O_3 as scaled to 1% decrease in global O_3 burden. In each part of this and subsequent figures, the dotted white line indicates the average pressure level of the MOZART tropopause. The nPB mixing ratio in Fig. 1a peaks at the emissions region with little reaching the Southern Hemisphere, and no more 10 ppt, or 2% of the 349 ppt maximum mixing ratio, reaches the tropopause. The mixing ratio of the degradation product BrAc, shown in Fig. 1b, peaks at 2.1 ppt near the surface, and the maximum BrAc mixing ratio at the tropopause is less than 0.02 ppt. However, the Br_y perturbation in the Northern Hemisphere exceeds 2.5 ppt for much of the lower stratosphere, as shown in Fig. 1c. The stratospheric Br_y perturbation in excess of nPB mixing ratios at the tropopause suggests that Br_y is

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the product gas group that enters the stratosphere, and the minimum Br_y perturbation in the tropics suggests that much of the Br_y crosses north of 20° N. nPB increases Br_y by at least 1 ppt everywhere in and above the MOZART stratosphere, and the O_3 perturbation percentage in Fig. 1d includes both a peak in the Northern polar upper troposphere and a secondary maximum near the South Polar tropopause with minimal O_3 loss in the tropics around 10 hPa. The atmospheric chemical lifetime obtained for nPB is 24.7 days, comparable to the value reported in Ko et al. (2003), and the chemical lifetime for BrAc is 5.4 h, consistent with the estimate of Burkholder et al. (2002). The ODP obtained for nPB is 0.0049, smaller than the value reported previously. This ODP is lower by a factor of more than three compared to the most comparable value reported in Table 2-12 of Ko et al. (2003), 0.017 for emissions from North America, Europe, and Asia with the correction for reduced BrAc using maximum rainout of Br_y species in Wuebbles et al. (2001). Atmospheric lifetimes and ODPs for nPB, TCE, and PCE obtained in this study are summarized in Table 1.

A study with nPB emissions of 2.90×10^8 molecules cm^{-2} s^{-1} evenly distributed over land surfaces from 60° S to 70° N, which totals 2.49 Tg yr^{-1} and is comparable to the "global" case in Wuebbles et al. (2001), was also conducted in MOZART-3. The nPB annual and zonal average mixing ratios, shown in Fig. 2a, show that penetration to the tropopause is more symmetric than for 30°–60° N emissions, and between 1 and 2.5 ppt of nPB reaches the tropopause at all latitudes northward of 25° S. While the BrAc distribution in Fig. 2b is also more symmetric than that for 30°–60° N nPB emissions, the peak mixing ratio is 0.43 ppt compared to a maximum nPB mixing ratio of 110 ppt in Fig. 2a, and the maximum tropopause BrAc mixing ratio is less than 0.005 ppt. The Br_y perturbation resulting from these nPB emissions, shown in Fig. 2c, is more than 2.5 ppt throughout much of the stratosphere up to the 10 hPa pressure layer, but the Br_y perturbation at the tropopause is smaller for 30° S to 30° N than for surrounding latitudes outside that range. As with Fig. 1a–c, this indicates that bromine from nPB in MOZART-3 enters the stratosphere mostly outside the tropics as Br_y. The O_3 percent loss for these emissions in Fig. 2d again peaks at either pole, but the South Polar

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tropopause is the maximum loss and the reduction in tropical tropospheric O_3 is greater than for 30°–60° N emissions in Fig. 1d. For the global emissions case, the derived atmospheric lifetime of nPB is 19.6 days, nearly the same as in Wuebbles et al. (2001), and the resulting ODP is 0.011, more than a factor of two lower than the global high wet-deposition ODP reported in Wuebbles et al. (2001) or the 0.027 value given in Ko et al. (2003) Table 2-12 for that Wuebbles et al. (2001) result after BrAc correction. The comparisons of current ODPs with the values reported in Ko et al. (2003) after BrAc correction indicate that O_3 in MOZART-3 is less sensitive to Br_y from nPB than was the case for the combination of MOZART-2 with the UIUC 2-D model as used in Wuebbles et al. (2001).

TCE is widely used as an industrial solvent; PCE (also called tetrachloroethylene) is commonly used in fabrics dry-cleaning, metal degreasing, as well as a feedstock for chemical manufacture. The MOZART-3 CTM with added surface flux for land from 30° N to 60° N is run to near-steady-state for each compound as with nPB fluxes. A PCE surface flux of 3.91 Tg yr^{-1} in MOZART-3 results in the annual and zonal average mixing ratio distribution shown in Fig. 3a. PCE reaches the tropical tropopause at a markedly higher fraction of the peak mixing ratio than for nPB (compare Fig. 1b). The tropopause PCE mixing ratios, which range from 100 ppt at the North Pole to 50 ppt at 40° S, are consistent with the stratospheric Cl_y perturbation of up to 0.35 ppb in Fig. 3b because each PCE molecule carries four chlorine atoms and because the small values of tropospheric Cl_y perturbation form a similar pattern to those from longer-lived chlorocarbons such as HCFC-123. PCE seems likely to transport Cl_y to the stratosphere as PCE by a combination of tropical and extra-tropical transport, unlike the case for Br_y from nPB. The global O_3 column perturbation is −0.344%, and Fig. 3c shows that O_3 loss from PCE occurs mostly at polar latitudes with a maximum loss in the South Polar lower stratosphere. The PCE atmospheric lifetime obtained is 111 days, and the ODP calculated for PCE in MOZART-3 is 0.0060, among the lowest of values obtained for any chlorocarbon so far.

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TCE was run at two surface fluxes for which the MOZART-3 results are summarized in Table 2. The initial run using 51.7 Tg yr^{-1} produced a global O_3 column decrease of 0.306% with an atmospheric lifetime of 13.8 days. Figure 4a shows the annual and zonal average TCE distribution for this flux peaks at 5750 ppt in the emissions region, and intact TCE transport to the stratosphere is limited to perhaps 0.1% even at the North Pole. The Cl_y perturbations (ppb) in Fig. 4b are concentrated in the emission region, with mixing of Cl_y from TCE along the extratropical Northern upper troposphere and into the stratosphere seemingly limited by rainout removal at North Polar latitudes below the 300 hPa pressure layer and effectively no change in Cl_y throughout most of the stratosphere and the Southern troposphere. The O_3 losses resulting from TCE, as shown in Fig. 4d, are mostly constrained to the Northern troposphere and range up to 40% reduction. Because this large TCE flux results in such a large change of O_3 at Northern latitudes, distortion of the OH field in MOZART-3 resulting in an overestimation of TCE lifetime is a possible concern. Therefore, we also ran with one-fourth that TCE flux, or 12.9 Tg yr^{-1}. The O_3 column perturbation was one-fourth that of the 51.7 Tg yr^{-1} run, and the TCE lifetime reported was 13.0 days, consistent with a minimal OH field perturbation from TCE, and we report the lifetime from the 12.9 Tg yr^{-1} run in Table 1. The TCE ODP, 0.00035, is unaffected to within 1% by the change of surface flux.

These ODP results suggest that known annual releases of these two chlorocarbons to the atmosphere, which as of 1999 totaled 0.146 Tg for TCE and 0.387 Tg for PCE in the Reactive Chlorine Emissions Inventory (McCulloch et al., 1999; Keene et al., 1999), should have less than 0.1% effects on global total ozone, and future applications of these compounds that do not exceed these fluxes should have similarly limited ozone effects.

Our MOZART-3 analyses of TCE and PCE have not considered possible degradation chemistry after the initial addition of OH, instead treating these compounds as if all Cl atoms were released within a model time step. TCE and PCE atmospheric degradation schemes have not been comprehensively evaluated by experiment, but a recent

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study (Nolan et al., 2006) indicates that some 70% of TCE and PCE reacting with OH produces phosgene ($COCl_2$) under atmospheric conditions. $COCl_2$ has negligible reactivity with gas-phase species in the troposphere and a 1.85 year lifetime against photolysis in the stratosphere (Kindler et al., 1995), suggesting that it could transport significant Cl from TCE or PCE to the stratosphere. However, $COCl_2$ hydrolyzes in liquid water (Sander et al., 2006, and references therein) so that this oxidation product could reduce total gas-phase Cl perturbations resulting from TCE or PCE. An additional TCE and PCE oxidation product likely to be produced by the mechanisms presented in Nolan et al. (2006) is hydrogen chloride (HCl), which is soluble in liquid water and readily adsorbed on ice. While HCl yield is not quantified in the Nolan et al. study, HCl removal by wet deposition would reduce the total Cl input to the atmosphere from TCE or PCE emissions. We believe that the TCE and PCE ODPs reported in this study are maximum values because of the possible production of HCl and $COCl_2$ by tropospheric degradation, each of which is subject to wet deposition.

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Table 1. Derived atmospheric lifetimes and ODPs.

Gas	Emission Latitudes	Lifetime, days	ODP
nPB	30° N–60° N	24.7	0.0049
nPB	60° S–70° N	19.6	0.011
TCE	30° N–60° N	13.0	0.00035
PCE	30° N–60° N	111	0.0060

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Table 2. Summary of lifetimes and ozone changes in MOZART-3 for two total surface fluxes of trichloroethylene (TCE) from 30° N to 60° N land surfaces.

TCE flux, Tg yr^{-1}	Lifetime, days	O_3 column change, %	ODP
12.92	13.0	−0.0769	0.00035
51.69	13.8	−0.306	0.00035

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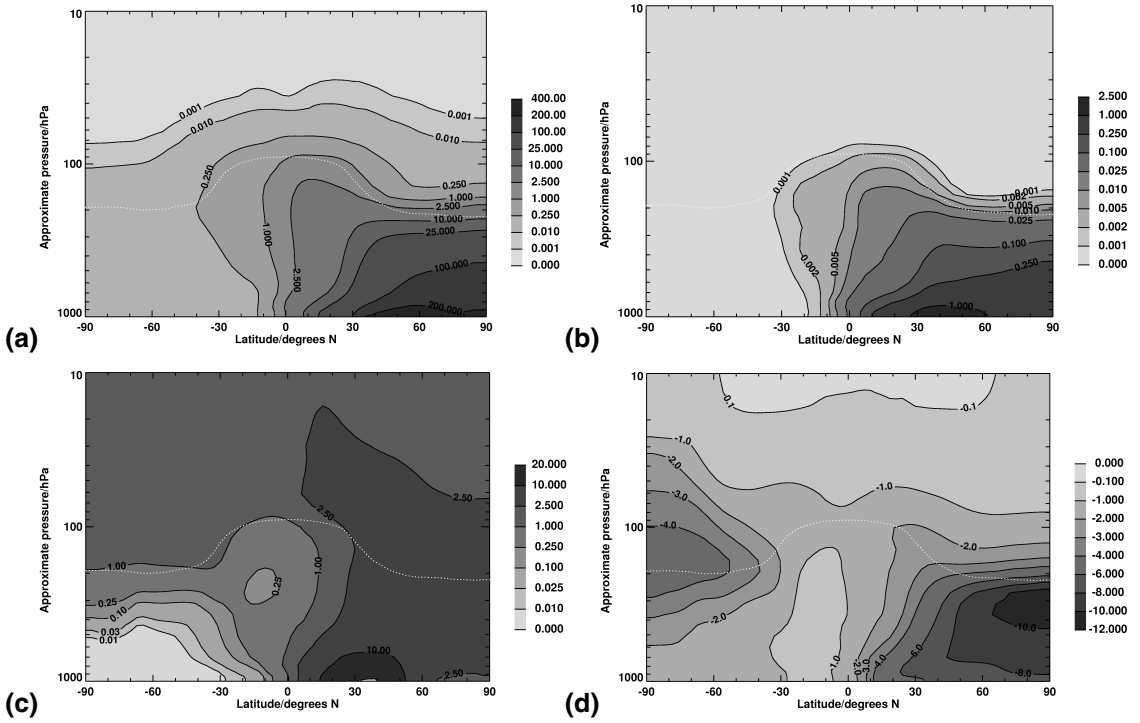

Fig. 1. Annual- and zonal-average mixing ratio changes calculated in MOZART-3 for n-propyl bromide (nPB) emissions evenly distributed on land surfaces from 30° N to 60° N totaling 2.48 Tg yr^{-1}. **(a)** nPB in ppt; **(b)** bromoacetone (BrAc) in ppt; **(c)** inorganic bromine species (Br_y) in ppt; **(d)** ozone (O_3) in percent.

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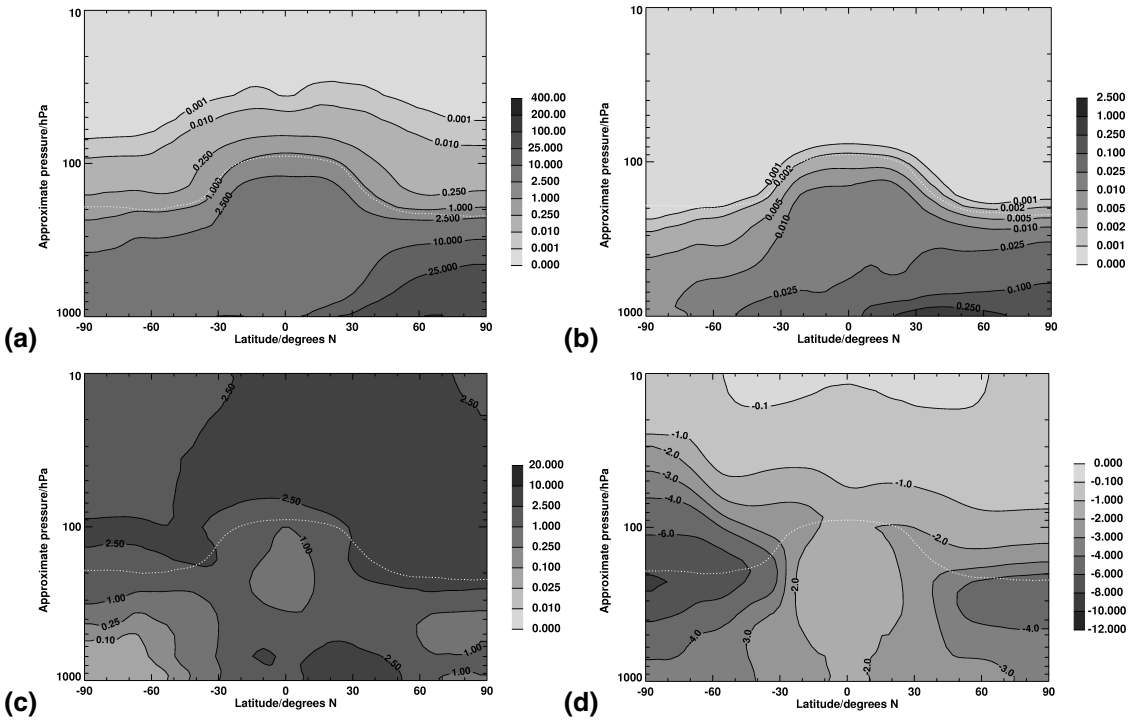

Fig. 2. Annual- and zonal-average mixing ratio changes calculated in MOZART-3 for nPB emissions evenly distributed on land surfaces from 60° S to 70° N totaling 2.49 Tg yr^{1}. **(a)** nPB in ppt; **(b)** BrAc in ppt; **(c)** Br_y in ppt; **(d)** O_3 in percent.

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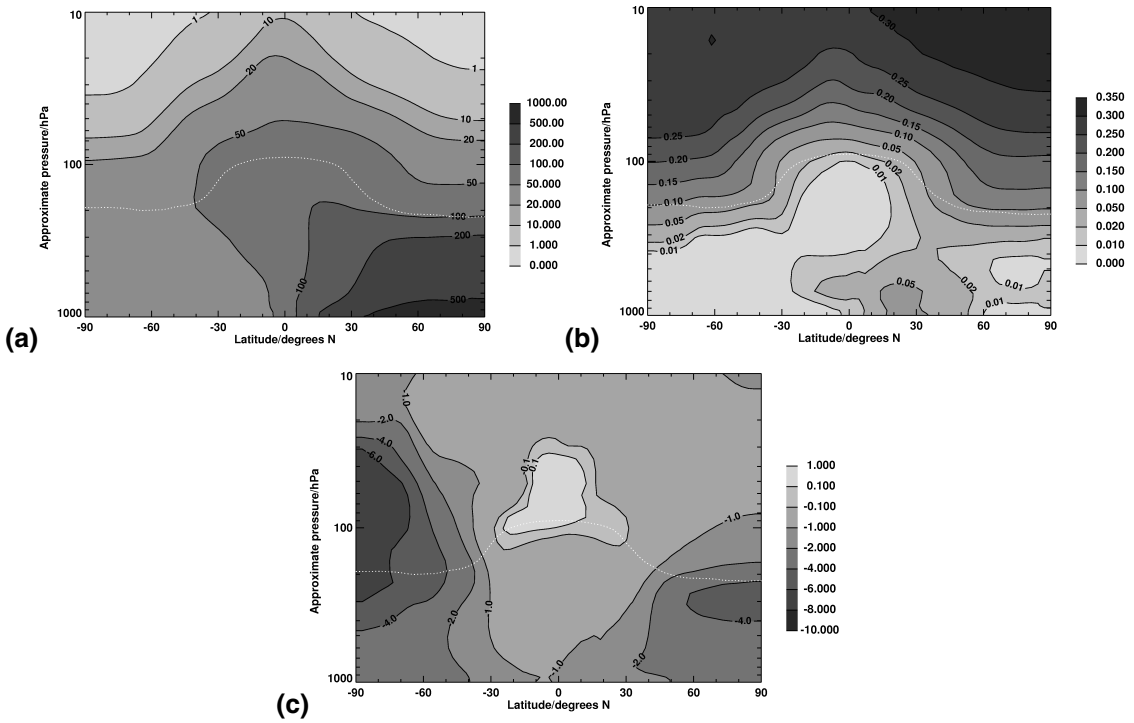

Fig. 3. Annual- and zonal-average mixing ratio changes calculated in MOZART-3 for perchloroethylene (PCE) emissions evenly distributed on land surfaces from 30° N to 60° N totaling 3.91 Tg yr^{-1}. **(a)** PCE in ppt; **(b)** Cl_y in ppb; **(c)** O_3 in percent.

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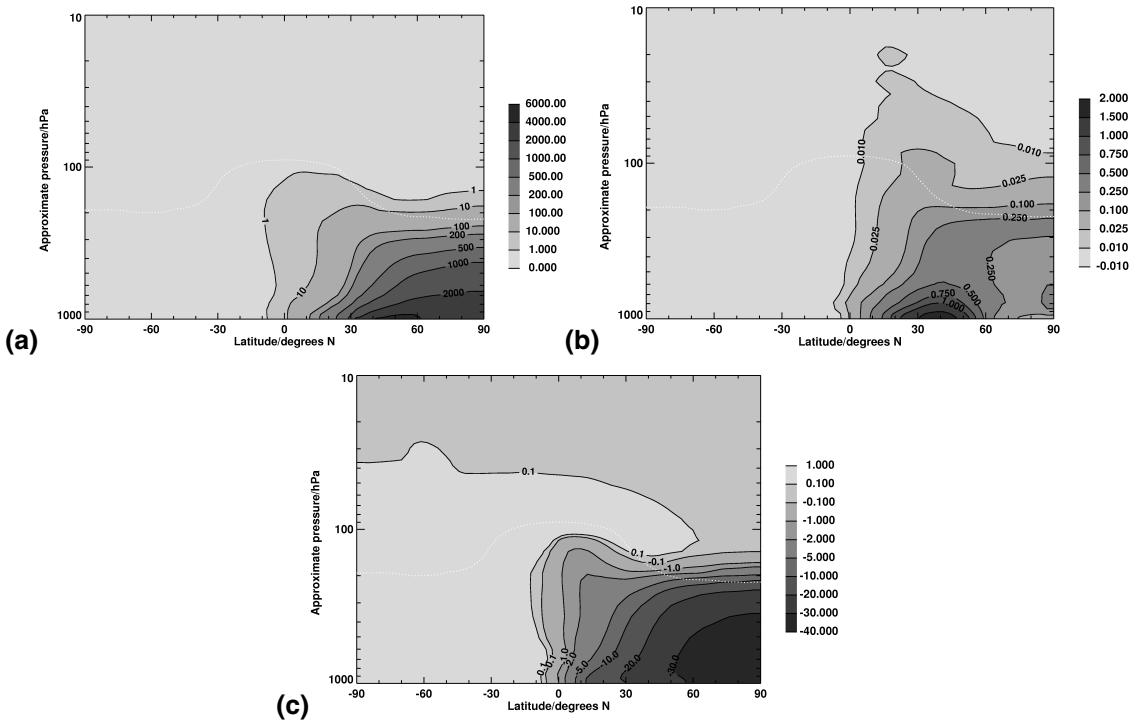

Fig. 4. Annual- and zonal-average mixing ratio changes calculated in MOZART-3 for trichloroethylene (TCE) emissions evenly distributed on land surfaces from 30° N to 60° N totaling 51.7 Tg yr^{-1}. **(a)** TCE in ppt; **(b)** inorganic chlorine species (Cl_y) in ppb; **(c)** O_3 in percent.

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3-D modeling of nPB, TCE, and PCE Ozone Depletion Potentials

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